

# Synthesis and Application of Novel Navel Orange Antistaling Agent

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**Abstract.** An effective carboxymethyl chitosan coating is developed for fresh-keeping of Gannan navel orange. The results show that 1.5% carboxymethyl chitosan and its compound is the best agent. The preservative can easily form thin coating. Effectively inhibit respiration rate and invasion of pathogens, so as to keep fruits fresh. The results show that the ascorbic acid, total sugar, organic acids of experimental group are much higher than those of control groups. This kind of preservative can effectively keep fruit fresh.

**Keywords:** Navel orange, carboxymethyl chitosan, and preservation

## 1. Introduction

Navel orange contain a variety of nutrients, and was deeply loved by the masses of consumers. But it deteriorated because of growth in the area of strong seasonal, and after harvest due to physical, physiological and pathological factors [1]. This brought economic disaster to the seller. Navel orange production rapid development in China, but as a result of preservation technology backward postpartum attrition rate is as high as 25% ~ 30% every year. So fruit postharvest storage is the guarantee of the peak season now, off-season continuously and meet the international demand [2]. Anniversary of the establishment of the market equilibrium the important link of the supply and agricultural production efficiency.

For a long time, low temperature, modified atmosphere, such as relief measures used drugs is a major way of navel oranges postharvest storage, but the long-term use of chemical agents can lead to virus resistant, more serious is that caused the increase of pesticide residues on the navel orange, endangering human health [3]. Therefore, becoming more and more attention in the development of natural, efficient, safe, non-toxic green fresh-keeping agent, stable performance.

Carboxymethyl chitosan is a natural polysaccharide found in large Numbers only in product of alkaline amino polysaccharide, chitosan derivative and generate. It has a unique set of properties and features: with avirulence, biocompatible, biodegradable, film-forming ability and antimicrobial properties. It has been widely used in agriculture, environmental protection, cosmetics, medicine, food and other fields [4]-[8]. This topic for the first time with carboxymethyl chitosan and its complexes of fresh navel orange was studied, the purpose is to look for a new type of green edible composite antistaling agent, provide technical support for fruit and vegetable coating preservation.

## 2. Materials and Methods

### 2.1. Materials and instruments

Navel orange (collected from jiangxi province ganzhou city economic and technological development zone navel orange orchard); Degree of chitosan (90.75%); The rest of the chemical reagents were analytical grade.

KQ3200B type constant temperature ultrasonic cleaning machine; Z89-1 type electric blender; DHG - 9073 bs - III thermostatic dryer drum wind; SHB - III circulating A multi-purpose vacuum pump, etc.

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## 2.2. Test method

- The preparation of carboxymethyl chitosan

To three neck flask adding chitosan, add in isopropyl alcohol, stirring, make its swelling. Add appropriate amount of NaOH solution into the above solution and stirring, let the chitosan in the center of the expansion form alkaline alkaline conditions. Will moderate solid chloroacetic acid points several times to join in the solution, every time interval of a few minutes, heated to a certain temperature, control the reaction time and mixture of carboxymethyl chitosan. Adjust pH to add distilled water in the solution, glacial acetic acid to the isoelectric point. Then filter, washed with ethanol, dry with oven.

- **Preservation of liquid preparation**

The above obtained good carboxymethyl chitosan is soluble in water, add a moderate amount of additives, mixture concentration were 1.0%, 1.5%, 2.0% of three fresh liquid, set aside.

- **The sample processing**

Randomly selected from each time about 10 kilograms of the same maturity degree, size uniformity, no plant diseases and insect pests and no mechanical damage on the surface of gannan navel orange fruit, respectively 1.0%, 1.5%, 2.0% of the fresh liquid and water soak 20 s, natural dry film-forming, packed into plastic crate, observation and experiment, test at room temperature, the results were compared with water treatment (CK).

## 2.3. Measurement method

Every 20 or 30 days investigation degree of rotting, andom sample determination of biochemical indicators.

- **Rotten fruit rate calculation:** the rotten fruit rate (%) = number of rotten fruit/total number of fruit x 100% (experiment fruit skin appear stain spots as rotten fruit).
- **Weightlessness rate determination:** weightlessness ratio = (weight - storage after weight before storage)/weight x 100% before storage
- **Vitamin C content in 2, 6-dichloro indophenol sodium method** [9].
- **Soluble total sugar content was measured by anthrone colorimetry** [10].
- **Organic acid titration neutralization with alkali.**
- **Breathing intensity determination:** the infrared CO<sub>2</sub> analyzer determination [11]. The indicators measuring repeat 3 times.

## 3. Results and Analysis

### 3.1. Effect of preservation of fresh-keeping agent for navel orange test.

- **Effects of carboxymethyl chitosan coating on Rotten fruit rate of navel orang**

Navel orange during storage led to the decay of the main pathogens are penicillium, chloramphenicol, doxycycline and rot. This experiment studied the antistaling agent to navel orange fungus inhibition. It can be seen from table 1 with different mass fraction of carboxymethyl chitosan preservative navel orange, in normal temperature storage for 140 days, on average, rotten fruit rate 3 times lower. That the carboxymethyl chitosan as the main body of the antistaling agent can effectively reduce the navel orange decay.

Table 1. Effects of carboxymethyl chitosan coating on Rotten fruit rate of navel orang

Mass fraction/%	Rotten fruit rate/number					
	10d	30d	50d	80d	110d	140d
CK	6	10	16	18	22	28
1.0	3	6	7	9	10	11
1.5	0	2	4	6	6	7
2.0	2	4	6	6	7	8

- **Effects of carboxymethyl chitosan coating on weight loss of navel orang**

Navel orange during storage will appear different degrees of weightlessness. This is navel orange lost goods value is one of the important factors. The table 2 shows that using the fresh-keeping agent of fruits during the whole storage weightlessness rate are lower than the control group. 30 days, the control fruit weight loss rate are increased obviously, 140 days of weightlessness rate reached to 8.6%. And obtained with fresh fruit weight loss rate in 50 before a significant change, which treated with 1.5% carboxymethyl

chitosan formula group of the weightlessness rate of change is most slowly, the weightlessness rate is only 3.6% in 140 days. That the carboxymethyl chitosan as the main body of the antistaling agent can effectively reduce the weightlessness of navel orange.

Table 2. Effects of carboxymethyl chitosan coating on weight loss of navel orange

Mass fraction/%	Weight loss /%					
	10d	30d	50d	80d	110d	140d
CK	0.3	0.8	2.3	3.2	5.1	8.6
1.0	0.2	0.4	1.3	2.2	3.1	5.2
1.5	0.2	0.3	0.8	1.6	2.5	3.6
2.0	0.2	0.4	1.1	2.0	2.8	4.6

• **Effects of carboxymethyl chitosan coating on concentrations of ascorbic acid of navel orange**

Vitamin C is an important nutrients in fruits and vegetables. The quantity of navel orange contains vitamin C is very high, but the navel orange during save easy to loss as oxidized. From table 3, using carboxymethyl chitosan treatment in the navel orange storage of 140 days, vitamin C content is 13.37% higher than the control group on average. That the carboxymethyl chitosan as the main body of the antistaling agent of navel orange vitamin C has certain protective effect. Carboxymethyl chitosan (1.5% mass fraction in the protective effect of vitamin C is most significant.

Table 3. Effects of carboxymethyl chitosan coating on concentrations of ascorbic acid of navel orange

Mass fraction/%	Ascorbic acid/mg (100g) <sup>-1</sup>					
	10d	30d	50d	80d	110d	140d
CK	58.76	54.87	51.29	46.36	42.12	38.06
1.0	57.95	56.56	54.78	52.15	50.26	48.67
1.5	58.80	58.46	57.27	56.39	55.18	53.62
2.0	58.38	57.65	55.91	54.22	53.18	52.01

• **Effects of carboxymethyl chitosan coating on concentrations of total sugar of navel orange**

It can be concluded that from table 4, When the fruits are fresh of Just picking, the higher content of total sugar in navel orange fruit. During the period of storage, total sugar content have experienced a process of change from small to big and small. Control group in total sugar content in fruit 50 d after reaching a maximum 12.1% was dropped significantly. And obtained with fresh fruits of the content of total sugar in 80 d reaches a maximum and then drops slowly. With 1.5% carboxymethyl chitosan treatment group, among them the slowest decrease total sugar content. Carboxymethyl chitosan as the main body of the antistaling agent can reduce the loss of total sugar content in the navel orange storage process.

Table 4. Effects of carboxymethyl chitosan coating on concentrations of total sugar of navel orange

Mass fraction/%	Total sugar/%					
	10d	30d	50d	80d	110d	140d
CK	11.8	11.9	12.1	11.8	11.6	11.3
1.0	11.6	11.7	11.9	12.2	12.0	11.8
1.5	11.8	11.9	12.2	12.3	12.2	12.1
2.0	11.5	11.7	11.9	12.1	11.9	11.7

• **Effects of carboxymethyl chitosan coating on concentrations of organic acids of navel orange**

Acid is the most easy to use fruit respiration substrates, it is the primary source of atp synthesis energy, at the same time is also necessary to many biochemical processes in the cell in the middle of the metabolites of the provider. As a result, the acid in the process of storage decreasing speed how fast directly reflects the strength of the respiration, also affected the fruit flavor and taste. The table 5 shows that the fruit acidity decreased gradually during room temperature storage. After treated with preservatives of navel orange 140 d, organic acid content is 22.67% higher than the control group. Carboxymethyl chitosan as the main body of the antistaling agent of organic acids in the navel orange storage process plays a protective role.

Table 5. Effects of carboxymethyl chitosan coating on concentrations of organic acids of navel orange

Mass fraction/%	Organic acids/%					
	10d	30d	50d	80d	110d	140d
CK	1.10	1.02	0.99	0.95	0.85	0.79
1.0	1.12	1.10	1.09	1.06	1.03	1.00
1.5	1.11	1.09	1.08	1.07	1.05	1.04
2.0	1.10	1.08	1.07	1.05	1.03	1.01

#### • Effects of carboxymethyl chitosan coating on respiration of navel orange.

Respiration intensity was used to measure a respiration intensity index, evaluation of fresh navel orange storage life of an important symbol, is the most important physical characteristics of navel orange. Storage of navel orange respiration is strong, quality drop, the more obvious, shorter shelf life is. As you can see in table 6, during the whole storage through preservation processing fruit fruit respiration intensity and control group were in decline after the first rising trend. Control fruit respiration intensity after the storage after the minimum value of 10.09 mg CO<sub>2</sub> (kg h)<sup>-1</sup>. After 140 days storage preservation treatment than with the control, the fruits of the respiration intensity, on average, 26.66% reduction. This suggests that with carboxymethyl chitosan as the main body of the antistaling agent can effectively inhibit the fruit inside and outside gas exchange, reduce endogenous O<sub>2</sub>/CO<sub>2</sub> ratio, thus inhibiting navel orange respiration, achieve good preservation effect.

Table 6. Effects of carboxymethyl chitosan coating on respiration of navel orange

Mass fraction/%	Respiration /mgCO <sub>2</sub> (kg h) <sup>-1</sup>					
	10d	30d	50d	80d	110d	140d
CK	33.21	28.15	35.36	19.05	17.48	15.38
1.0	27.56	23.06	25.38	17.80	15.16	11.07
1.5	26.37	22.26	24.56	16.21	14.37	10.09
2.0	2.0	28.22	24.31	25.36	18.24	15.96

### 3.2. Futher preservation mechanism are discussed

Carboxymethyl chitosan molecules containing large amounts of hydroxyl and carbonyl, soluble in water, form a transparent film on the fruit surface. Because of carboxymethyl chitosan of the groups in molecules, make it has the very high water and moisturizing effect, at the same time also can block pathogen metabolic or directly kill pathogenic bacteria, prevent hyphae formation of, reduce pathogenic bacteria infection, thus delay the wilting and rot.

Is good film forming properties of carboxymethyl chitosan physical and chemical basis of fruit with good preservation effect. Carboxymethyl chitosan on the fruit surface forming a layer similar to cellulose membrane, reducing oxygen partial pressure inside the fruit, reduce the consumption of material transformation and respiratory substrate in fruit, have the similar gas packaging effect.

With different concentration of carboxymethyl chitosan solution, its viscosity is different, is different, in terms of formation of the plastic wrap film has distinct effect on the quality of preservation of the length of time. When the concentration of carboxymethyl chitosan is less than 1.0, the film is thinner, its gas exchange on navel orange fruit inside with the air resistance is small, result in higher concentration of oxygen in the fruit, respiration increase, nutrient consumption relatively quickly, the effect is bad; When more than 2.0%, the film is too thick, the navel orange fruit in the oxygen concentration is too low, cannot satisfy the normal breathing, so the preservation time is shortened; Only appropriate concentration (1.5%) of the coating handling navel orange, form the film thickness is appropriate, can both aerobic respiration, and prevents moisture loss too fast, storage time is prolonged, thereby achieve preservation.

## 4. Conclusion

Experiments show that the carboxymethyl chitosan as the main body of the preservatives in carboxymethyl chitosan mass fraction was 1.5%, can well inhibit the respiration intensity of navel orange, reduce fruit decay rate, make the fruit rot rate 3 times lower than the control group, vitamin c, total sugar, organic acid content were significantly higher than the control group, which reduces the navel orange fruit in the loss of nutrients in normal temperature storage process, good preservation effect.

Carboxymethyl chitosan as a new type of green edible composite antistaling agent, has low cost. It has many advantages such as low cost, safe non-toxic, environmental protection, easy to operate, etc. Fresh navel oranges were kept in a common room at room temperature. When eating fruit for washing can be removed dissolved. According to people demand for fruit preservation security, it has a good application prospect.

## 5. References

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